

(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号
特開2000-282032
(P2000-282032A)

(43) 公開日 平成12年10月10日 (2000. 10. 10)

(51) Int.Cl. ⁷	識別記号	F I	テマコード* (参考)
C 0 9 K 11/71	C P W	C 0 9 K 11/71	C P W 4 H 0 0 1
11/63	C P K	11/63	C P K
11/70	C P W	11/70	C P W
11/73	C P W	11/73	C P W

審査請求 未請求 請求項の数 2 書面 (全 3 頁)

(21) 出願番号	特願平11-126210	(71) 出願人	599059977 株式会社太平洋経済開発 東京都豊島区駒込 2-12-1・A-I I 2 F
(22) 出願日	平成11年3月30日 (1999. 3. 30)	(72) 発明者	庄 学 海 中国上海市董家渡路17号 2-278
		F ターム (参考)	4H001 CF02 XA04 XA05 XA08 XA12 XA14 XA15 XA20 XA30 XA38 XA48 XA56 YA25 YA50 YA51 YA57 YA58 YA60 YA63 YA65 YA66 YA67 YA69 YA83

(54) 【発明の名称】 蓄光性蛍光体組成物

(57) 【要約】

【課題】一般式 $aT_o \cdot bT' \cdot cSiO_2 \cdot dQ : Eu_x, K_y$ で示される組成物でどのような可視光線でも容易に励起され、蓄光性に優れると共に残光輝度も高く、色調が豊富で、且つ耐水性に優れた蓄光性蛍光体組成物を提供すること。

【解決手段】従来の蓄光性蛍光体組成物の母結晶の主成分であるアルミ酸に代わって、シリコン酸塩を母結晶の主成分とし、これに Sr 、 Ca 、 Ba 、 Zn の酸化物、 Mg 、 Cd 、 Be の元素、及び B_2O_3 、 P_2O_5 をそれぞれの群より少なくとも一種以上混合して母結晶を構成し、賦活剤としてユーロピウム、共賦活剤として Nd 、 Dy 等の金属元素を配合して焼成、焼結することによって課題を解決した。

【特許請求の範囲】

【請求項1】 一般式 $a\text{To} \cdot b\text{T}' \cdot c\text{SiO}_2 \cdot d\text{Q} : \text{Eu}_x, \text{K}_y$ で示される蓄光性蛍光体組成物で、ここでTがSr、Ca、Ba、Znの元素の少なくとも一種以上から、T'がMg、Cd、Beの元素の少なくとも一種以上から、Qが B_2O_3 、 P_2O_5 の一種以上から、KがNd、Dy、Ho、Tm、La、Pr、Tb、Ce、Mn、Bi、Sn、Sbの元素の少なくとも一種以上からなるもので、a、b、c、d、x、yの値がモル値で、それぞれ、 $1 \leq a \leq 3$ 、 $1 \leq b \leq 3$ 、 $0.5 \leq c \leq 9$ 、 $0.01 \leq d \leq 0.3$ 、 $0.0001 \leq x \leq 0.2$ 、 $0 \leq y \leq 0.3$ であることを特徴とする蓄光性蛍光体組成物。

【請求項2】 請求項1で示した組成物を水素ガス濃度15～25%に定めた水素ガスと窒素ガスの混合ガス中で、1000～1600℃の焼成温度で、1～60時間焼結して得られた蓄光性蛍光体組成物。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、蓄光性蛍光体組成物に関するものであり、その利用分野は玩具、文具などの生活用品分野から建築、土木、船舶などの工業分野まで幅広く利用されるもので最近特に安全用品分野までの利用に注目が集まっている。

【0002】

【従来の技術】蓄光性蛍光体組成物の歴史は長く、古くは19世紀後半に発明された硫化亜鉛系組成物が有名であるが、賦活剤として用いるCoの放射性障害の安全性や大気中の安定性に不安があり、黒化、分解するという欠点を有していた。これらの問題点を解決するために考案されたアルミ酸を母結晶とする蓄光性組成物（特公平-2543825）があるが、耐水性に乏しいこと、更には発光ピーク波長が短波長側にしか見られず、色調が限られるなどの課題点、問題点を残していた。

【0003】

【本発明が解決しようとする課題】従来の技術でも述べたように、本発明は安全、耐候性に優れ、更には強靱な耐水性を付与すると共に、従来の技術では不可能であった色調の広範化、即ち発光ピーク波長を可視光線波長の全域に拡大し、多種色の新たな蓄光性蛍光体組成物を提供しようとする物である。

【0004】

【課題を解決するための手段】前記課題を解決するため、本発明者達は、鋭意研究を重ねた結果、蓄光性蛍光体組成物の母結晶を、シリコン酸塩を主成分とし、これに種々の元素或いは酸化物を添加して構成し、賦活剤としてユウロビウム（Eu）を用い、更に共賦活剤としてNd、Dy、Ho、Tm、La、Pr及びTbの中から少なくとも一種以上を添加することにより、前記課題を解決できることを見出し、本発明を完成するに至った。

共賦活剤として、更にCe、Mn、Bi、Sn、或いはSbを用いることもできる。母結晶の主成分はシリコン酸塩であるが、これに、更にSr、Ca、Ba或いはZnの酸化物を1種以上添加し、更にはこれにMg、Cd或いはBeの元素を一種以上添加し、更に加えて B_2O_3 、或いは P_2O_5 を一種以上添加して母結晶の安定化を図り、耐水性の飛躍的向上を見ることができた。

【0005】

【発明の実施の形態】何故、このような特徴を出せたかについての詳細は定かではないが、基本的にはシリコン酸塩を母結晶の主成分に導入したことが本発明をもたらしたと推察される。本発明のシリコン酸塩を主成分とする母結晶にSr、Ca、Ba或いはZnの化物及びMg、Cd或いはBeの元素、及び B_2O_3 、或いは P_2O_5 の一種以上を共晶させることにより、母結晶の安定性が、飛躍的に向上したと言える。賦活剤として用いる元素はEuのみであるが、共賦活剤として用いるNd、Dy、Ho、Tm、La、Pr及びTbの効果により、更には、共賦活剤として用いる可能なCe、Mn、Bi、Sn、或いはSbを添加することにより従来の蓄光性蛍光体組成物の励起波長を250～400nmの短波長光線から、可視光線である400～700nmにシフトできた。従って、本発明が提供した蓄光性蛍光体組成物は、私達が感知できる光であれば十分な蓄光効果が得られ、発光するピーク波長も450～650nmと極めて可視光線波長に近いことから、種々の色を発光するのが特徴である。即ち、蛍光灯や白熱灯下でも充分な蓄光性が見られ、発光する色も青、青緑、緑、黄緑、黄と多種におよぶことができた。本発明によって提供することができる蓄光性蛍光体組成物は、請求範囲で示した組成物の混合粉末を水素及び窒素の混合ガス中の還元雰囲気中で、1000～1600℃に加熱し、1～60時間保持して得る事ができる。混合ガス中の水素ガス濃度が15～25である。水素ガス濃度が15%以下では水蒸気などの酸化性ガスの影響を受け、組成物が酸化されて良好な蓄光性蛍光体組成物を得ることができない。また、その濃度が25%以上になると組成物中の酸化物が還元されてしまい、これもまた良好な蓄光性蛍光体組成物を得る事ができない。焼成温度、保持時間についても同様のことが言える。1000℃以下では良好な焼結体を得られず、1600℃以上では還元雰囲気の影響が顕著になり、組成物が還元されて、目的とする良好な組成物を得ることができない。保持時間が1時間以下だと、本発明の低温度領域に当たる1000℃付近では焼結が不完全でもろい組成物しか得られないばかりか、混合粉末の均質化を図ることができず、良好な蓄光性蛍光体組成物を得る事ができない。60時間以上の保持時間では組成物自体では良好なものもできるが、エネルギーの無駄使いになり、製造コストも上がってしまう。

【0006】

【実施例】本発明の効果を実施例、比較例を示しながら更に詳細に説明する。一般式 $aT_o \cdot bT' \cdot cSiO_2 \cdot dQ : Eu_x, K_y$ における a 、 b 、 c 、 d 、 x 、 y を以下の表のように定め、更に T 、 T' 、 K 、 Q を定

めて、実施例 1～3 を示した。本発明の効果を確認するため、比較例 1～3 を同時に示して得られた蓄光性蛍光体の蓄光性、色調及び耐水性を比較した。

	実施例 1	実施例 2	実施例 3
a	1	2	3
b	1	2	3
c	0.5	8	1
d	0.02	0.1	0.2
x	0.0002	0.1	0.2
y	0	0.1	0.3
T	Sr	Ba	Ca, Zn
T'	Mg	Be	Mg, Be
K	Ce	Dy	Ho, Dy
Q	B ₂ O ₃	B ₂ O ₃ , P ₂ O ₅	B ₂ O ₃
比較例 1	SrAl ₂ O ₄ : Eu, Dy		
比較例 2	SrAl ₂ O (Al ₂ O ₃) : Eu, Dy		
比較例 3	CaAl ₂ O ₄ : Eu, Dy		

実施例及び比較例のそれぞれの混合組成粉末を 20% 水素濃度の水素+窒素の混合ガス雰囲気で、1220℃で 8 時間焼結し蓄光性蛍光体組成物を得た。それぞれの組成物を 200 ルックス、4 分間、D₆₅ 常用光線を用い

て励起し、10 分後の残光輝度 (mcd/m²) を測定するとともに、その色調と水中に 1 日間浸漬後の組成物の状態を観察し、変化のないものを○、やや崩れているものを△、完全に崩れているものを×で表した。

	実施例			比較例		
	1	2	3	1	2	3
残光輝度 mcd/m ²	280	250	270	260	100	1
色 調	青	緑	黄	緑	青緑	青紫
耐水性	○	○	○	×	×	×

【0007】

【発明の効果】以上で明らかなように、一般式 $aT_o \cdot bT' \cdot cSiO_2 \cdot dQ : Eu_x, K_y$ で示された組成物は、それぞれの係数である a 、 b 、 c 、 d 、 x 、 y 及び成分である T 、 T' 、 Q 、 K を特許請求範囲に示した数値及び成分で構成して、1000～1600℃、水

素濃度 15～20% の水素+窒素の混合ガス中で 1～60 時間を焼成、焼結することによって、通常の可視光線で容易に励起されて、色調が豊富で残光輝度が大きく、しかも耐水性が良好な蓄光性蛍光体組成物を得ることができる。

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2000-282032

(43)Date of publication of application : 10.10.2000

(51)Int.Cl.

C09K 11/71

C09K 11/63

C09K 11/70

C09K 11/73

(21)Application number : 11-126210

(71)Applicant : TAIHEIYO KEIZAI KAIHATSU:KK

(22)Date of filing : 30.03.1999

(72)Inventor : SHO GAKUKAI

(54) LUMINOUS FLUOPHOR COMPOSITION**(57)Abstract:**

PROBLEM TO BE SOLVED: To obtain the subject composition capable of easily exciting any visible light, excellent in luminous capacity and high in afterglow luminance as well, rich in color tone, and high in water resistance.

SOLUTION: This luminous fluophor composition is shown by the general formula $aT.bT'.cSiO_2.dQ:Eux, Ky$ (T is at least one element selected from Sr, Ca, Ba and Zn; T' is at least one element selected from Mg, Cd and Be; Q is at least one compound selected from B₂O₃ and P₂O₅; K is at least one element selected from Nd, Dy, Ho, Tm, La, Pr, Tb, Ce, Mn, Bi, Sn and Sb; (a), b, c, d, x and y satisfy the relationships: $1 \leq a \leq 3$, $1 \leq b \leq 3$, $0.5 \leq c \leq 9$, $0.01 \leq d \leq 0.3$, $0.0001 \leq x \leq 0.2$, and $0 \leq y \leq 0.3$ (mol)). This luminous fluophor composition is obtained by the following practice: using a silicate as the main component of the matrix crystal in place of an aluminate as the main component of the matrix crystal in conventional luminous fluophor compositions, the silicate is mixed with at least one of the respective oxides of Sr, Ca, Ba and Zn, at least one element of Mg, Cd and Be, and at least one oxide selected from B₂O₃ and P₂O₅ to construct the matrix crystal, which is then incorporated with europium as activator and a metallic element such as Nd or Dy as coactivator followed by carrying out a burning and sintering.

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CLAIMS

[Claim(s)]

[Claim 1]The general formula $aTo-bT'$ with a phosphorescent-materials constituent shown by $-cSiO_2$ and $dQ:Eu_x$, and K_y . An element of Sr, Ca, Ba, and Zn at least here from more than a kind. [T] Even if an element of Mg, Cd, and Be has little T', a kind, as mentioned above Q B_2O_3 . A kind of P_2O_5 , as mentioned above K are the things of an element of Nd, Dy, Ho, Tm, La, Pr, Tb, Ce, Mn, Bi, Sn, and Sb which consist of more than a kind at least, A phosphorescent-materials constituent in which a value of a, b, c, d, x, and y is characterized by being $1 \leq a \leq 3$, $1 \leq b \leq 3$, $0.5 \leq c \leq 9$, $0.01 \leq d \leq 0.3$, $0.0001 \leq x \leq 0.2$, and $0 \leq y \leq 0.3$ with a mol value, respectively.

[Claim 2]A phosphorescent-materials constituent produced by sintering for 1 to 60 hours with calcination temperature of 1000-1600 ** in mixed gas of hydrogen gas which provided a constituent shown by claim 1 in 15 to 25% of hydrogen gas concentration, and nitrogen gas.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which an invention belongs and to carry out] This invention relates to a phosphorescent-materials constituent.

The field of the invention is broadly used from the consumer-goods fields, such as a toy and stationery, to the industrial fields, such as construction, engineering works, and a marine vessel, and attentions have gathered for use to the safe article field especially recently.

[0002]

[Description of the Prior Art]Although the history of the phosphorescent-materials constituent was long and the zinc sulfide system constituent invented in ancient times in the second half of the 19th century was famous, the safety of the postirradiated lesion of Co used as an activator and the stability in the atmosphere have anxiety, and it had melanism and the fault of decomposing. Although there was a light storing constituent (Japanese Patent Publication No.-2543825) which uses as a mother crystal the aluminum acid devised in order to solve these problems, it being lacking in a water resisting property and also an emission peak wavelength were seen only at the short wavelength side, but it had left technical-problem points — a color tone is restricted — and a problem.

[0003]

[Problem(s) to be Solved by the Invention]As the Prior art also described, this invention is excellent in safety and weatherability, and gives a still tougher water resisting property, and it is a thing which is going to expand extensive-ization of the impossible color tone, i.e., an emission peak wavelength, throughout visible light wavelength, and is going to provide the new phosphorescent-materials constituent of a variety color in a Prior art.

[0004]

[Means for Solving the Problem]In order to solve said technical problem, as a result of this invention persons' repeating research wholeheartedly, a mother crystal of a phosphorescent-materials constituent, Use silicon acid chloride as the main ingredients, and various elements or oxides are added and constituted in this, Using a europium (Eu) as an activator, by adding more than a kind at least out of Nd, Dy, Ho, Tm, La, Pr, and Tb as a coactivator, it finds out that said technical problem is solvable, and came to complete this invention. As a coactivator, Ce, Mn, Bi, Sn, or Sb can also be used. Although the main ingredients of a mother crystal are silicon acid chloride, To this, one or more sorts of oxides of Sr, Ca, Ba, or Zn are added further, More than a kind was able to add an element of Mg, Cd, or Be to this, in addition, more than a kind was able to add B₂O₃ or P₂O₅ further, stabilization of a mother crystal was able to be attained, and waterproof improvement in fast was able to be found.

[0005]

[Embodiment of the Invention]Although the details about the ability of such a feature to have been taken [why] out are not certain, it is guessed that having introduced silicon acid chloride into the main ingredients of the mother crystal fundamentally brought about this invention. The stability of a mother crystal can say that it improved by leaps and bounds by carrying out the eutectic crystal of more than a kind of the element of the ghost of Sr, Ca, Ba, or Zn and Mg, Cd, or Be and B₂O₃, or P₂O₅ to the mother crystal which uses the silicon acid chloride of this invention as the main ingredients. Although the element used as an activator is only Eu, As a coactivator, by the effect of Nd, Dy, Ho, Tm and La to be used, Pr, and Tb further, The excited wavelengths of the conventional phosphorescent-materials constituent have been shifted from a 250-400-nm short-wavelength-light line to 400-700 nm which is visible light by adding possible Ce used as a coactivator, Mn, Bi, Sn, or Sb. Therefore, if the phosphorescent-materials constituent which this invention provided is the light which we can detect, it is the feature that sufficient light storage effect is acquired and the peak wavelength which emits light also emits light in various colors from that 450-650 it is nm and it being very close to visible light wavelength. That is, light storing sufficient also in the bottom of a fluorescent lamp or an incandescent lamp was seen, and the color which emits light was also able to attain to blue, bluish green, green, yellowish green, yellow, and a variety. The phosphorescent-materials constituent which can be provided by this invention heats the powder mixture of the constituent shown by the generic claim at 1000-1600 ** by the reducing atmosphere in the mixed gas of hydrogen and nitrogen, and it can obtain it by the ability to hold it for 1 to 60 hours. The hydrogen gas concentration in mixed gas is 15-25. Hydrogen gas concentration cannot be influenced by oxidizing gases, such as a steam, at 15% or less, a constituent cannot oxidize, and a good phosphorescent-materials constituent cannot be obtained. If the concentration will be not less than 25%, the oxide in a constituent will be returned, and this cannot obtain a good phosphorescent-materials constituent, either. It can say that the same may be said of calcination temperature and retention time. Below 1000 **, a good sintered compact is not obtained, above 1600 **, the influence of reducing atmosphere becomes remarkable, a constituent is returned, and the good target constituent cannot be obtained. If retention time is 1 or less hour, near 1000 ** which is equivalent to the low-temperature degree field of this invention, sintering cannot attain uniformity of only an imperfect and weak constituent not only being obtained but powder mixture, and cannot obtain a good phosphorescent-materials constituent. In the retention time of 60 hours or more, a good thing is made at the constituent itself, and it will be a waste of ENERUKI and a manufacturing cost will also go up.

[0006]

[Example]The effect of this invention is explained still in detail, while an example and a comparative example are shown.

General formula $aT_0-bT'_1a$ in $-cSiO_2$ and $dQ:Eu_x$, and K_y , b, c, d, x, and y were defined as shown in the following tables, and also T, T', K, and Q were defined, and Examples 1-3 were shown. In order to check the effect of this invention, the light storing of the phosphorescent materials produced by showing the comparative examples 1-3 simultaneously, the color tone, and the water resisting property were compared.

	実施例 1	実施例 2	実施例 3
a	1	2	3
b	1	2	3
c	0.5	8	1
d	0.02	0.1	0.2
x	0.0002	0.1	0.2
y	0	0.1	0.3
T	Sr	Ba	Ca、Zn
T'	Mg	Be	Mg、Be
K	Ce	Dy	Ho、Dy
Q	B ₂ O ₃	B ₂ O ₃ 、P ₂ O ₅	B ₂ O ₃
比較例 1	SrAl ₂ O ₄ :Eu, Dy		
比較例 2	SrAl ₂ O (Al ₂ O ₃):Eu, Dy		
比較例 3	CaAl ₂ O ₄ :Eu, Dy		

Each mixture composition powder of the example and the comparative example was sintered at 1220 ** for 8 hours by the mixed gas atmosphere of hydrogen + nitrogen of 20% hydrogen concentration, and the phosphorescent-materials constituent was obtained. A D₆₅ common beam of light is used for each constituent for 200 luxs and 4 minutes. While exciting and measuring the afterglow brightness of 10 minutes after (mcd/m²). The state of the constituent after immersion was observed for one day to [the / color tone and underwater], O and a little collapsed thing were expressed with **, and the thoroughly collapsed thing was expressed with x for that changeless.

	実施例			比較例		
	1	2	3	1	2	3
残光輝度 mcd/m ²	280	250	270	260	100	1
色 調	青	緑	黄	緑	青緑	青紫
耐水性	○	○	○	×	×	×

[0007]

[Effect of the Invention]The constituent shown by general formula $aT_0-bT'_1a$, $cSiO_2$ and $dQ:Eu_x$, and K_y above so that clearly, Q and K are constituted from T and T' which are a, b, c, d, x, y, and the ingredient which are each coefficient, a numerical value shown in the claim, and an ingredient. By calcinating and sintering 1 to 60 hours in 1000-1600 ** and the mixed gas of hydrogen + nitrogen of 15 to 20% of hydrogen concentration, it is easily excited by ordinary visible light, and a color tone is abundant, afterglow brightness is large, and, moreover, a phosphorescent-materials constituent with a good water resisting property can be obtained.

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EFFECT OF THE INVENTION

[Effect of the Invention]The constituent shown by general formula aT_o-bT' , $cSiO_2$ and $dQ:Eu_x$, and K_y above so that clearly, Q and K are constituted from T and T' which are a, b, c, d, x, y, and the ingredient which are each coefficient, a numerical value shown in the claim, and an ingredient. By calcinating and sintering 1 to 60 hours in 1000-1600 ** and the mixed gas of hydrogen + nitrogen of 15 to 20% of hydrogen concentration, it is easily excited by ordinary visible light, and a color tone is abundant, afterglow brightness is large, and, moreover, a phosphorescent-materials constituent with a good water resisting property can be obtained.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention]As the Prior art also described, this invention is excellent in safety and weatherability, and gives a still tougher water resisting property, and it is a thing which is going to expand extensive-ization of the impossible color tone, i.e., an emission peak wavelength, throughout visible light wavelength, and is going to provide the new phosphorescent-materials constituent of a variety color in a Prior art.

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MEANS

[Means for Solving the Problem]In order to solve said technical problem, as a result of this invention persons' repeating research wholeheartedly, a mother crystal of a phosphorescent-materials constituent, Use silicon acid chloride as the main ingredients, and various elements or oxides are added and constituted in this, Using a europium (Eu) as an activator, by adding more than a kind at least out of Nd, Dy, Ho, Tm, La, Pr, and Tb as a coactivator, it finds out that said technical problem is solvable, and came to complete this invention. As a coactivator, Ce, Mn, Bi, Sn, or Sb can also be used. Although the main ingredients of a mother crystal are silicon acid chloride, To this, one or more sorts of oxides of Sr, Ca, Ba, or Zn are added further, More than a kind was able to add an element of Mg, Cd, or Be to this, in addition, more than a kind was able to add B_2O_3 or P_2O_5 further, stabilization of a mother crystal was able to be attained, and waterproof improvement in fast was able to be found.

[0005]

[Embodiment of the Invention]Although the details about the ability of such a feature to have been taken [why] out are not certain, it is guessed that having introduced silicon acid chloride into the main ingredients of the mother crystal fundamentally brought about this invention. The stability of a mother crystal can say that it improved by leaps and bounds by carrying out the eutectic crystal of more than a kind of the element of the ghost of Sr, Ca, Ba, or Zn and Mg, Cd, or Be and B_2O_3 , or P_2O_5 to the mother crystal which uses the silicon acid chloride of this invention as the main ingredients. Although the element used as an activator is only Eu, As a coactivator, by the effect of Nd, Dy, Ho, Tm and La to be used, Pr, and Tb further, The excited wavelengths of the conventional phosphorescent-materials constituent have been shifted from a 250-400-nm short-wavelength-light line to 400-700 nm which is visible light by adding possible Ce used as a coactivator, Mn, Bi, Sn, or Sb. Therefore, if the phosphorescent-materials constituent which this invention provided is the light which we can detect, it is the feature that sufficient light storage effect is acquired and the peak wavelength which emits light also emits light in various colors from that 450-650 it is nm and it being very close to visible light wavelength. That is, light storing sufficient also in the bottom of a fluorescent lamp or an incandescent lamp was seen, and the color which emits light was also able to attain to blue, bluish green, green, yellowish green, yellow, and a variety. The phosphorescent-materials constituent which can be provided by this invention heats the powder mixture of the constituent shown by the generic claim at 1000-1600 ** by the reducing atmosphere in the mixed gas of hydrogen and nitrogen, and it can obtain it by the ability to hold it for 1 to 60 hours. The hydrogen gas concentration in mixed gas is 15-25. Hydrogen gas concentration cannot be influenced by oxidizing gases, such as a steam, at 15% or less, a constituent cannot oxidize, and a good phosphorescent-materials constituent cannot be obtained. If the concentration will be not less than 25%, the oxide in a constituent will be returned, and this cannot obtain a good phosphorescent-materials constituent, either. It can say that the same may be said of calcination temperature and retention time. Below 1000 **, a good sintered compact is not obtained, above 1600 **, the influence of reducing atmosphere becomes remarkable, a constituent is returned, and the good target constituent cannot be obtained. If retention time is 1 or less hour, near 1000 ** which is equivalent to the low-temperature degree field of this invention, sintering cannot attain uniformity of only an imperfect and weak constituent not only being obtained but powder mixture, and cannot obtain a good phosphorescent-materials constituent. In the retention time of 60 hours or more, a good thing is made at the constituent itself, and it will be a waste of ENERUKI and a manufacturing cost will also go up.

[0006]

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EXAMPLE

[Example]The effect of this invention is explained still in detail, while an example and a comparative example are shown. General formula $aT_0-bT'a$ in $-cSiO_2$ and $dQ:Eu_x$ and K_y , b, c, d, x, and y were defined as shown in the following tables, and also T, T', K, and Q were defined, and Examples 1-3 were shown. In order to check the effect of this invention, the light storing of the phosphorescent materials produced by showing the comparative examples 1-3 simultaneously, the color tone, and the water resisting property were compared.

	実施例 1	実施例 2	実施例 3
a	1	2	3
b	1	2	3
c	0.5	8	1
d	0.02	0.1	0.2
x	0.0002	0.1	0.2
y	0	0.1	0.3
T	Sr	Ba	Ca, Zn
T'	Mg	Be	Mg, Be
K	Ce	Dy	Ho, Dy
Q	B ₂ O ₃	B ₂ O ₃ , P ₂ O ₅	B ₂ O ₃
比較例 1	SrAl ₂ O ₄ :Eu, Dy		
比較例 2	SrAl ₂ O(Al ₂ O ₃):Eu, Dy		
比較例 3	CaAl ₂ O ₄ :Eu, Dy		

Each mixture composition powder of the example and the comparative example was sintered at 1220 ** for 8 hours by the mixed gas atmosphere of hydrogen + nitrogen of 20% hydrogen concentration, and the phosphorescent-materials constituent was obtained. A D₆₅ common beam of light is used for each constituent for 200 luxs and 4 minutes. While exciting and measuring the afterglow brightness of 10 minutes after (mcd/m²), The state of the constituent after immersion was observed for one day to [the / color tone and underwater], O and a little collapsed thing were expressed with **, and the thoroughly collapsed thing was expressed with x for that changeless.

	実施例			比較例		
	1	2	3	1	2	3
残光輝度 mcd/m ²	280	250	270	260	100	1
色 調	青	緑	黄	緑	青緑	青紫
耐水性	○	○	○	×	×	×

[Translation done.]